

July 31, 1996

Mr. Clem Zidick
RR1, Box 767
Wabeno, WI 54566

RE: Crandon Mine & Chromium Disposition

Dear Mr. Zidick:

On May 23, 1996 you had sent me several documents (all enclosed for return to you as requested) regarding and supporting your concern regarding the fate of chromium at the Crandon Mine site within the Tailings Management Area (TMA). You had also included responses to your concern from William Tans, WDNR, and with Jerome Goodrich, Crandon Mining Company (CMC). Both Mr. Tans and Mr. Goodrich responded to your concern but you were not satisfied with their responses and requested that the U.S. EPA review your material for another opinion. Mr. John Morris, a chemist within U.S. EPA's Central Regional Laboratory, reviewed your material and other resources that he had available to him. His review is attached. Briefly, he states that your concern is valid but not probable in the scenario most likely to be present within the TMA of the Crandon Mine Project. His reasonings are detailed in his attached response. What he did recommend, however, and that I will follow through with and include in on U.S. EPA's subsequent comments on CMC's Environmental Impact Report and on both the state and federal Environmental Impact Statements, is that the pH must be continuously monitored within the TMA and that the leachate from the TMA should be analyzed for chromium (which presently has not been proposed by CMC).

I want to thank you for your involvement in highlighting this issue to the WDNR and to the U.S. EPA. If you have further information regarding this issue or any other issue regarding the project, or have questions regarding this review, I would be glad to hear from you; please feel free to give me a call at (312) 886-7252.

Sincerely,

Daniel J. Cozza
U.S. EPA Crandon Mine Project Manager

July 31, 1996 Mr. Clem Zidick

enclosures:

cc:
William Tans, WDNR

Ken Fish, Menominee

Don Moe, CMC
Sonny Wreczycki,
John Koss, Menominee
Dave Ballman, COE
Ron Spry, U.S. FWS
Jim Krohelski, U.S. GS
Mark Kuester, U.S. BIA
Ann McCammon, GLIFWC

Greg Bunker, Stockbridge-Munsee
John Coleman, GLIFWC
John Griffin, Mole Lake
Kathy Condon, Menominee
Steve Dodge, EPA
Llewellyn Boyd, Menominee
Herb Nelson, U.S. BIA
Christine Hansen, FCP

Attachment:

**UNITED STATES ENVIRONMENTAL PROTECTION
AGENCY
REGION V
CENTRAL REGIONAL LABORATORY**

Date: December 6, 2002

Subject: Mr. Clement Zidick's Commentary on the Fate of Chromium at Crandon Mine

From: John V. Morris, Chemist
Central Regional Laboratory

To: Daniel Cozza, Team Leader
Crandon Mine Team

I conducted a review of the documents supplied by Mr. Clement Zidick with regard to the fate of chromium at Crandon Mine. What I have concluded from this review is that what Mr. Zidick contends is possible, but is not probable. For the chromium to be resuspended at high pH, enough lime must be added to the tailings pond to raise the pH to 11 or 12, in spite of the acid generated by the sulfide and ferrous iron oxidation. In order for the resuspended chromium to be reoxidized to the hexavalent state, all of the sulfide and ferrous iron, which are competing for any oxidizing agent, must be oxidized.

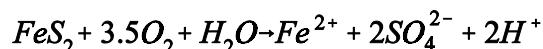
It is my opinion that the pH should be monitored during the liming process to insure that the pH will not exceed 8. It most likely will not, except for some localized effects where mixing has not occurred. I will leave design of any monitoring scheme to the engineers. Perhaps the leachate should be monitored for total chromium. This may not be any burden, as it will probably be monitored for other metals anyway. I would not require that the leachate be monitored for hexavalent chromium, unless it can be shown that the leachate is not a reducing medium. This could be demonstrated by a spike recovery measurement for Cr(VI) on the leachate. If the spike is not recovered, one should not expect Cr(VI) to exist in the samples. Should any work be done on hexavalent chromium analysis of the leachate, and if the leachate is turbid or colored, I would recommend a chromatographic

technique such as Method 218.6. If the leachate is neither turbid nor colored, the less expensive colorimetric method may be used.

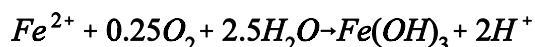
The review document prepared earlier is attached.

Mr. Clem Zidick of Wabeno, Wisconsin has raised an issue over the use of $\text{Na}_2\text{Cr}_2\text{O}_7$ at Crandon Mine in the flotation process for separation of lead and copper ores. His argument is that the subsequent chromium removal process by addition of lime is not adequate, stating that significant amounts of Cr(III), which is precipitated as $\text{Cr}(\text{OH})_3$, will be resolubilized at high pH, through the quaternary complex $\text{Cr}(\text{OH})_4^-$. In addition, he is of the opinion that dissolved oxygen could reconvert the Cr(III) back to Cr(VI), posing a greater health risk.

It is true that at a high pH, formation of $\text{Cr}(\text{OH})_4^-$ is significant ($\log K_4 = 29.9$)¹. The question becomes whether the pH will get high enough for this to occur. With a saturated solution of $\text{Ca}(\text{OH})_2$, which CaO hydrolyzes to form, it is possible to obtain a pH of 12. The problem is that this is not so simple a system. The presence of pyrites (FeS_2) in the process produce acid from the oxidation of both the ferrous iron and the sulfide. The common reactions which produce acid mine drainage are:²



and



These reactions, in addition to producing acid, consume the dissolved oxygen that might react with Cr(III) to produce Cr(VI). Virtually all groundwater systems that contain S^{2-} are anoxic. This results in adsorption or coprecipitation of trace metals.³

J. A. Dean, ed. "Lange's Handbook of Chemistry", 12th edition, (McGraw-Hill, New York) p. 5-51, (1979).

J. I. Drever, "The Geochemistry of Natural Waters," (Prentice-Hall, Englewood Cliffs, NJ) p. 62 (1982).

J. Hong, W. Calmano, and U. Förstner, Chapter 6 in "Trace Elements in Natural Waters", B. Salbu and E. Steinnes, eds. (CRC Press, Boca Raton, FL) (1995).

The reverse case, that of oxic soils and sediments, are dominated by easily reduced manganese oxides,^{3,4} sometimes referred to as δ - MnO_2 . In oxic soils and sediments, chromium oxidation has been documented.⁴ In a study of absorption of Cr(VI) to soils, application of lime to the soils decreased the amount absorbed and later recovered by an extractant.⁵ The liming in this case increased the soil pH from around 5 to 7. A companion study whereby Cr(III) in a tannery waste was added to oxic soils containing manganese oxides found that more soluble Cr(III) chelates were formed in limed soils than unlimed.⁶ Still, the pH of the limed soils in these studies was never greater than 7.5. Another study of absorption of chromium from landfill leachate by clay minerals as a function of pH found that Cr(III) was completely absorbed above pH 6, and showed no desorption up to pH 9, while absorption of Cr(VI) dropped to near zero above pH 8.5.⁷ The pH of the clay was adjusted between 1 and 9 with HNO_3 and NaOH . None of these studies considered a situation where the pH went as high as 12.

Given all of the above, what are the merits and inconsistencies of the arguments by the various parties involved in the correspondence between Mr. Zidick and WDNR and the Crandon Mining Company? Mr. Zidick has presented some chemical arguments for what *could* occur at high pH, but the question is *can* the lime treatment achieve that high a pH with all the other chemistry that is going on. The anoxic sulfidic milieu that predominates in an acid mine drainage situation generates acid, scavenges dissolved oxygen, and provides reducing agents. The acid counteracts the lime, and the reduction provided by the sulfide and ferrous iron tends to react with the Cr(VI) to produce Cr(III). Even so, there is a lot of theoretical speculation and little real data is presented by either side. Even the EPA report⁸ quoted by the Foth and Van Dyke memorandum examines chromium spiked into an acid mine drainage matrix, and that only at a very narrow range of concentrations. It would be interesting to see real monitoring data from the facility, both for pH in the liming process, and Cr in the discharge.

R. Bartlett and B. James, *J. Environ. Qual.*, **8**, 31-35 (1979).

B. R. James and R. J. Bartlett, *J. Environ. Qual.*, **12**, 177-181 (1983).

B. R. James and R. J. Bartlett, *J. Environ. Qual.*, **12**, 173-176 (1983).

R. A. Griffin, A. K. Au, and R. R. Frost, *J. Environ. Sci. Health*, **A12**, 431-449 (1977).

EPA, 600/7-79-101, "Removal of Trace Elements from Acid Mine Drainage", (1979).

Sodium silicate, Na_2SiO_3 , which Mr. Zidick raises many questions about, is often used in wastewater treatment as a flocculent. This helps to precipitate solids and facilitate their removal.

Mr. Zidick's inclusion of the qualitative analysis scheme (exhibit 9a) has no bearing on the matter, because, although it shows the oxidation of $\text{Cr}(\text{OH})_3$ to CrO_4^{2-} in basic media, hydrogen peroxide is used to accomplish this. No one has indicated that such an oxidizing agent might be present in the mill process water. If it were, it would have to oxidize all the S^{2-} and Fe^{2+} first.